

## Insoluble Anodes for Copper Foil Production (II): Inhibition of PbO<sub>2</sub> Formation

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An insoluble anode consisting of an IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> catalytic layer formed on a titanium substrate has been increasingly used for oxygen evolution in electroplating industries such as electrogalvanizing and electroplating of steel. The excellent properties such as a high catalytic activity and a long lifetime in acidic media [1,2] have driven further applications in industrial electrolysis; one of them is copper foil production. Since the electrolyte used in copper foil production is based on sulfuric acid similar to that in electrogalvanizing of steel, it had been expected to possess a high durability for the application of the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti electrode replacing a previously used Pb alloy electrode. Although the actual consumption rate of the catalytic layer was not high when the electrode was applied for copper foil production, the electrode's lifetime for the continuous electrolysis in copper plating bath was shortened by another reason except the degradation of the catalytic layer, as mentioned below. The copper plating bath contains Pb(II) ions as a impurity, which is easily oxidized to PbO<sub>2</sub> on the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti electrode during oxygen evolution. This causes the increase in oxygen overpotential, since the generated PbO<sub>2</sub> covers the catalytic layer. Moreover, the reduction of PbO<sub>2</sub> to PbSO<sub>4</sub> occurs on the electrode, resulting in a non-conductive film formed on the catalytic layer. This situation seriously affects the electrode's lifetime, thereby the continuous production of copper foil is disturbed.

Our laboratory attempted to make clear the reason for the formation of PbSO<sub>4</sub> and developed the method to avoid the reduction of PbSO<sub>4</sub> by controlling oxygen evolution potential [3]. However, a better approach to inhibit the PbSO<sub>4</sub> generation is to suppress the oxidation of Pb(II) to PbO<sub>2</sub> on the anode. For this purpose, we prepared IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti electrodes by thermal decomposition at different temperatures and investigated the electrode's behaviors for oxygen evolution and the oxidation of Pb(II) in this study.

The IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti electrodes were prepared by thermal decomposition of the coating solution containing Ir(IV) and Ta(V) on a titanium substrate. Thermal decomposition was carried out at different temperatures ranging from 613K to 743K. The anodic polarization behavior of each electrode was studied using HNO<sub>3</sub> solutions with and without Pb(NO<sub>3</sub>)<sub>2</sub> or using H<sub>2</sub>SO<sub>4</sub> solutions with and without PbSO<sub>4</sub>. The HNO<sub>3</sub>-based solutions were mainly utilized to study the oxidation behavior of Pb(II) ions, since the solubility of Pb(II) ions in the HNO<sub>3</sub>-based solutions is high, although PbSO<sub>4</sub> hardly dissolves in H<sub>2</sub>SO<sub>4</sub> solutions. A constant current electrolysis in the Pb(NO<sub>3</sub>)<sub>2</sub> solution was also conducted to know the amount of the anodically deposited PbO<sub>2</sub> on each electrode.

Figure 1 shows the effects of thermal decomposition temperature on the amount of PbO<sub>2</sub> deposited in the Pb(NO<sub>3</sub>)<sub>2</sub> solution. The result indicates that the oxidation of Pb(II) to PbO<sub>2</sub> is more suppressed at lower temperatures of thermal decomposition, especially at 673K or less. The inhibited deposition of PbO<sub>2</sub> on the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode prepared at the low temperatures was also confirmed in the PbSO<sub>4</sub> solution. These results suggest that the problem of PbO<sub>2</sub> deposition and the undesirable reduction to PbSO<sub>4</sub> on the IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/Ti anode in copper foil production can be successfully resolved by preparing the electrode at low temperatures below 673K.

Cyclic voltammetry was performed to discuss the mechanism

for the variation in the amount of PbO<sub>2</sub> with thermal decomposition temperature. The comparison of the voltammograms of the electrodes prepared at different temperatures in the HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub> solution without Pb(II) revealed that oxygen evolution was more promoted with decreasing temperature, because of the increase in the real surface area of the electrode, which was implied by the increase in the double layer capacitance. The cyclic voltammograms recorded in the Pb(NO<sub>3</sub>)<sub>2</sub> solution also showed that the anodic wave corresponding to the oxidation of Pb(II) to PbO<sub>2</sub> disappeared when the temperature was lowered, suggesting that the overpotential for the PbO<sub>2</sub> deposition becomes higher. The deposition overpotential was determined by cathodic linear sweep voltammetry following immediately after potentiostatic electrolysis in the Pb(NO<sub>3</sub>)<sub>2</sub> solution at different potentials. The result demonstrated that the deposition overpotential actually increased when the temperature was reduced.

Lowering thermal decomposition temperature induced the variation in the crystallographic structure and morphology of IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> catalytic layers. These variations are quite important to understand the mechanism for the enhanced oxygen evolution and the suppressed PbO<sub>2</sub> deposition, which will be also presented in this paper.

### References

1. R. Otagawa, M. Morimitsu, and M. Matsunaga, Nippon Kagaku Kaishi, No.5, p.299 (2000).
2. R. Otagawa, H. Shimizu, T. Inoue, M. Morimitsu, and M. Matsunaga, in the Proceedings of 9th Continuous Steel Strip Plating Sym., pp.11-16, AESF, (1999).
3. A. Matsuo, M. Morimitsu, M. Yamamura, R. Otagawa, and M. Matsunaga, in the paper presented at this meeting (2004).

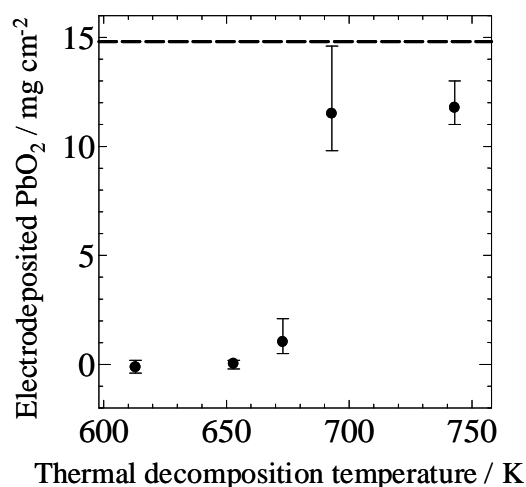


Fig. 1 Effects of the thermal decomposition temperature on the amount of PbO<sub>2</sub> deposited. The amount of electrodeposited PbO<sub>2</sub> with 100% current efficiency is also indicated (dash line).